A Molecular Box Derived from Cobaloxime Units Held Together by 4-Pyridinylboronic Acid Residues

Renata Dreos,* Giorgio Nardin, Lucio Randaccio,* Patrizia Siega, Giovanni Tauzher, and Višnja Vrdoljak†

Dipartimento di Scienze Chimiche, Università di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy

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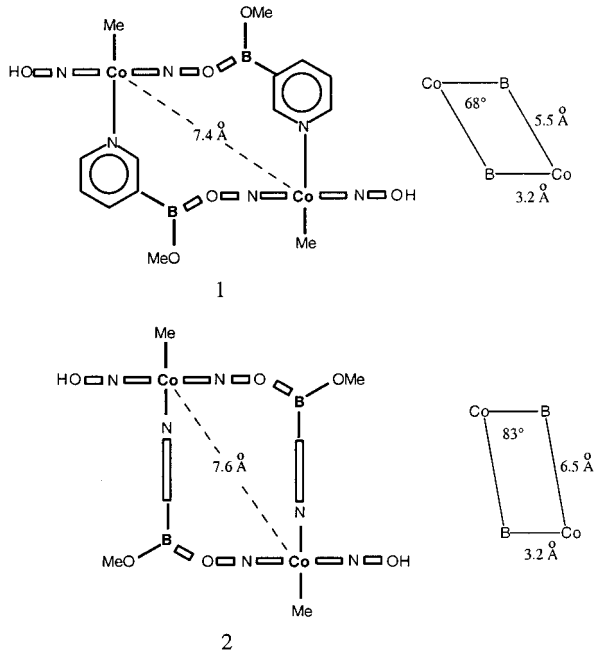
The reaction of $CH_3Co(DH)_2H_2O$ with 4-pyridinyl boronic acid in methanol or water affords the dinuclear complexes $[MeCo(DH)(DB(OR)(4\text{-}Py))]_2$, with R = Me (**2**) or H (**3**), respectively, through reaction of boron with the oxime oxygens of the alkylcobaloxime and coordination of the pyridinyl N to cobalt. The reaction is strongly pH dependent, and the formation of the complexes requires a neutral medium. The complexes have been fully characterized by ^1H and ^{13}C NMR spectroscopy, ESI-MS spectrometry, and elemental analysis. The X-ray structure shows that in **2**, the pyridinyl groups are facing each other and nearly perpendicular both to the plane of the Co B Co1 B1 atoms and to the mean equatorial plane, so that the complex may be considered a molecular box. A dimeric arrangement has already been found in the related $[MeCo(DH)(DB(OMe)(3\text{-}Py))]_2$ (**1**) complex, which forms a distorted molecular rectangle [Dreos, R.; Nardin, G.; Randaccio, L.; Tauzher, G.; Vuano, S. *Inorg. Chem.* **1997**, *36*, 2463]. The dimerization is possible in both cases, as the conformational freedom of the B bridge compensates for the different position (3- or 4-) of the pyridinyl N donor.

Introduction

Spontaneous self-assembly of cyclic metal complexes with right angles at their corners represents an area of great interest. In general, the metal units are at the vertexes of a square, with the bifunctional ligand forming the walls ("molecular box"). Alternatively, the ligands are at the corners and the metal units are along the edges ("molecular squares").[1]

We recently[2] reported that boronic acids containing pyridinyl substituents, such as $3\text{-}PyB(OH)_2$, may act as templates in the synthesis of polinuclear complexes through the reaction of the acid residue with the O··H··O bridges of alkylcobaloximes and the coordination of the pyridinyl group to metal. In fact, the ability of the BPh_2 group to substitute either one or both of the bridging H in cobaloximes (to form mono- or di-borylated alkylcobaloximes),[3] coupled with the Py coordination to cobalt, led to the formation of the dicobalt species $[MeCo(DH)(DB(OMe)(3\text{-}Py))]_2$, **1**. This species may be considered to be a distorted "molecular rectangle" ("molecular parallelogram") having two B and two Co atoms at the opposite corners. Two pyridinyl residues are on two opposite edges (nearly coplanar with the plane of the Co_2B_2 unit) with cobaloxime units on the other two edges, perpendicular to the Co_2B_2 plane (Scheme 1, compound **1**). When $4\text{-}PyB(OH)_2$ is used instead of the 3-Py isomer, a similar reaction occurs, with formation of the $[MeCo(DH)(DB(OMe)(4\text{-}Py))]_2$ compound (**2**), which is a "molecular box". The synthesis and the solution and solid-state characterization of **2** is reported and discussed.

Scheme 1



Experimental Section

General Information. UV−visible spectra were obtained with a Perkin-Elmer Lambda 5 spectophotometer. NMR spectra were recorded

* To whom correspondence may be addressed.

† Current address: Laboratory of General and Inorganic Chemistry, Chemistry Department, Faculty of Science, University of Zagreb. Ul. Kralja Zvonimira 8, 10 001 Zagreb, Croatia.

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on a JEOL EX-400 (^{1}H at 400 MHz and ^{13}C at 100.4 MHz). TMS was used as internal standard for ^{1}H and ^{13}C spectra, and $BF_3.Et_2O$ was used as external standard for ^{11}B spectra. Electrospray mass spectra were recorded in positive mode using an API 1 mass spectrometer (Perkin-Elmer) at 60 V cone voltage. EI mass spectra were recorded on a Micromass V6 7070 H mass spectrometer at 70 V.

The glassware used in synthesis of 4-pyridinyl boronic acid was dried at 200 °C overnight and cooled under a stream of nitrogen immediatly before use. Diethyl ether was dried on KOH and then distilled from sodium benzophenone. $CH_3Co(DH)_2H_2O$ was prepared according to literature techniques.[4] All other reagents were reagent grade and used without further purification.

Synthesis of 4-Pyridinyl Boronic Acid. 4-Bromopyridine hydrochloride (5.5 g, 28 mmol) was suspended in pentane (50 mL) and cooled to 0 °C in a water/ice bath. Triethylamine (4.4 mL, 32 mmol) was added, and the suspension was stirred for 8 h. The resulting triethylamine hydrochloride was filtered off, and the ethereal solution was evaporated in vacuo. The viscous oil thus obtained was poured into a flask containing freshly distilled diethyl ether (50 mL) and Na_2SO_4.

Diethyl ether (100 mL) was directly distilled into a flask equipped with a magnetic stirrer and a septum inlet. The solvent was degassed under nitrogen, maintained under a positive pressure of gas, and cooled at −110 °C in a liquid nitrogen/pentane bath. *n*-BuLi (1.6 M in hexane, 22.1 mL, 35.3 mmol) and TMEDA (*N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylendiamine) (5.3 mL, 35.3 mmol) were added by means of hypodermic syringes. 4-Bromopyridine was dropped into the solution over 0.5 h using the double needle technique, under nitrogen, and keeping the temperature at −110 °C. Finally, trimethylborate (4 mL, 35.3 mmol) was added drop by drop with a syringe. A white precipitate formed, and the suspension was allowed to reach room temperature and stirred under nitrogen overnight. The precipitate recovered by filtration was crude boronic acid contaminated by inorganic impurities, presumably LiOH, Li salts, and borates. To separate them, the crude product was redissolved in ethanol and the undissolved material filtered off. The white solid recovered by evaporation of the solvent in vacuo was dissolved in absolute ethanol with an equimolar amount of glacial acetic acid. The solution was refluxed for 4 h, and a white precipitate formed. A second fraction was collected by partial evaporation of the solvent. The solid obtained was almost pure 4-pyridinyl boronic acid (total yield about 34%), which was characterized by electron spray mass spectrometry (ESI−MS), electronic ionization mass spectrometry (EI−MS), elemental analysis, and NMR spectroscopy. Anal. Calcd for $C_5H_6NBO_2$: C, 48.8; H, 4.9; N, 11.4. Found: C, 47.7; H, 4.9; N, 11.1. ESI−MS (H_2O): m/z^+ calcd for $C_5H_6NBO_2$, 122.919; found, [M + H$^+$] 124.1. EI−MS: 123 (M$^+$), 106 (M$^+$ − H_2O), 105 (M$^+$ − OH$^-$), 79 (M$^+$ − HBO_2), 52 (79 − HCN). ^{1}H NMR (D_2O): δ 8.45(ortho), 8.07-(meta); (D_2O/$DClO_4$) 8.68 (ortho), 8.23 (meta); (D_2O/NaOD) 8.27 (ortho), 7.49 (meta). ^{13}C NMR: δ (D_2O) not soluble enough, (D_2O/$DClO_4$) 141.9 (ortho), 133.2 (meta); (D_2O/NaOD) 149.3 (ortho), 129.7 (meta). ^{11}B NMR: δ (D_2O) not soluble enough; (D_2O/$DClO_4$) 19.8; (D_2O/NaOD) 1.9.

Synthesis of [CH_3Co(DH)(DB(OMe)(4-Py))]$_2$ (2). $CH_3Co(DH)_2H_2O$ (0.3 g, 1 mmol) dissolved in methanol (25 mL) was added to 4-pyridinyl boronic acid (0.15 g, 1.2 mmol), and the pH of the solution was adjusted to 6.5 with $HClO_4$ 70%w/w. The yellow precipitate formed was filtered and washed with methanol. X-ray quality crystals were obtained by diffusion in methanol of a chloroform solution of the complex in the presence of 1% formic acid. Anal. Calcd for $C_{30}H_{46}N_{10}B_2O_{10}Co_2$: C, 42.6; H, 5.5; N, 16.5. Found: C, 40.6; H, 5.2; N,15.8. ESI−MS (CH_3-CN/HCOOH 1%): m/z^+ calcd for $C_{30}H_{46}N_{10}B_2O_{10}Co_2$, 846.246; found [M+ H$^+$], 848. ^{1}H NMR: ($CDCl_3$) δ 0.93 (6H, s, C*H*3 ax), 2.32 (12 H, s, CH_3C═NOH), 2.52 (12 H, s, CH_3C═NOB), 3.23 (6H, s, OCH_3) 6.67−6.72 (8H, m, pyridine protons). ^{13}C NMR ($CDCl_3$): δ 12.29 (*C*H_3C═NOH), 13.37 (*C*H_3C═NOB), 50.63 (O*C*H_3), 129.4 (meta of py), 144.9 (ortho of py), 148.0, 155.8 (*C*═N).

Synthesis of [CH_3Co(DH)(DB(OH)(4-Py))]$_2$ (3). The complex was synthesized in the same way as **2**, using water instead of methanol as solvent. ESI−MS (CH_3CN/HCOOH 1%): m/z^+ calcd for $C_{28}H_{42}N_{10}B_2O_{10}Co_2$, 818.18; found, [M+ H$^+$] 819.2. ^{1}H NMR: ($CDCl_3$) δ 0.93 (6H, s, CH_3 ax), 2.32 (12 H, s, CH_3C═NOH), 2.52 (12 H, s, CH_3C═NOB), 6.67−6.73 (8H, m, pyridine protons). ^{13}C NMR ($CDCl_3$): δ 12.30 (*C*H_3C═NOH), 13.45 (*C*H_3C═NOB), 129.4 (meta of py), 145.1 (ortho of py), 148.0, 155.8 (C═N).

Table 1. Crystal Data and Structure Refinement for **2**

formula	$C_{15.83}$ $H_{28.17}$ B Co N_5 O_8	fw	486.33
a	14.337(9) Å	space group	$P2_1/c$ (n° 14)
b	10.232(5) Å	*T*	293(2) K
c	16.405(9) Å	λ	0.71073 Å
β	115.20(3)°	ρ_{calcd}	1.483 g cm^{-3}
V	2177.5(21) Å^3	μ	0.840 mm^{-1}
Z	4	*R*, R_w [a]	0.0961, 0.2414

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

Equilibrium Studies. The deprotonation constants of 4-pyridinyl boronic acid were determined by spectrophotometric titration at 245.2 nm. A 10^{-3} M solution of acid in water at 25 °C, initially at pH about 10, was titrated with $HClO_4$ 1N by means of a microsyringe. The pK_{a1} was obtained from a plot of $\log[(A - A_0)/(A - A_\infty)]$ versus pH, in the pH range 10.0−6.0 (A_0 is the absorbance of anionic form of the acid, *A* the absorbance of the solution under examination, and A_∞ the absorbance of the neutral species in equilibrium with the zwitterionic form). The A_∞ value has been obtained as intercept from a plot of *A* versus $(A - A_0)/[H^+]$. The pK_{a2} was obtained from a plot of $\log[(A - A_0)/(A - A_\infty)]$ versus pH, in the pH range 5.0−2.0 (A_0 is the absorbance of the neutral species in equilibrium with the zwitterionic form, *A* the absorbance of the solution under examination, and A_∞ the absorbance of the cationic form of the acid).

Structure Determination of (2). One prismatic crystal, protected in a glass capillary tube, was used for data collection on a CAD4 automated diffractometer with graphite monochromated Mo Kα radiation. Correction for Lorentz polarization and φ scan absorption was applied. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares (on F^2), with anisotropic thermal parameters for all non-hydrogen atoms and the crystallization solvent molecules. The H atoms were not refined but were included at calculated positions in the final refinement. Crystal collection and refinement data are given in Table 1. The programs used are given in ref 5. Selected bond lengths and angles are listed in Table 2.

Results and Discussion

Synthesis of 4-Pyridinyl Boronic Acid. The synthesis of 4-pyridinyl boronic acid by reaction of *n*-butyllithium with 4-Br-pyridine and successive addition of trimethoxyborane at −60 °C has been previously described,[6] but with this procedure we obtained a very low yield. Furthermore, to our knowledge, the compound has not yet been fully characterized. The main problems in the synthesis arose from nucleophilic additions to 4-BrPy, which are competitive with the halogen metal exchange reaction at the relatively high temperature of −60 °C,[7] and from the low reactivity of 4-pyLi toward trimethoxyborane. To avoid these drawbacks, we lowered the temperature to −110 °C and added TMEDA (*N*,*N*,*N*′,*N*′ tetramethyl-1,2-ethylendiamine) as an activating agent. Both elemental analysis and mass spectra indicated that 4-pyridinyl boronic acid was isolated in the neutral form, $NC_5H_4B(OH)_2$.

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(5) (a) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838. Sheldrick, G. M. SHELXS-86, Program for Structure Solution. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. Sheldrick, G. M. SHELXL-93, Program for Structure Refinement; Universität Göttingen, Göttingen, Germany, 1993.

(6) (a) Fischer, F. C.; Havinga, E. *Recl. Trav. Chim. Pays Bas* **1974**, *93*, 21. (b) Fischer, F. C.; Havinga, E. *Recl. Trav. Chim. Pays Bas* **1965**, *84*, 439.

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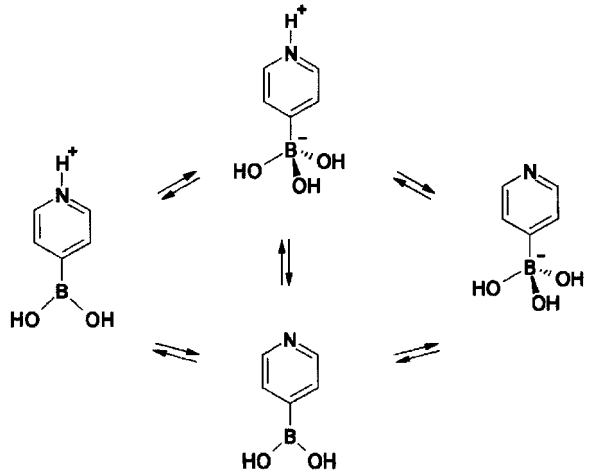
Table 2. Selected Bond Distaces (Å) and Angles (deg) for **1** and **2**

compound	**1**	**2**
Co−N1	1.872(7)	1.86(1)
Co−N2	1.862(8)	1.87(1)
Co−N3	1.868(8)	1.85(1)
Co−N4	1.872(7)	1.88(1)
Co−N51	2.068(8)	2.08(1)
Co−N14	1.99(1)	2.00(1)
Co····Co1	7.365(3)	7.592(5)
Co····B	3.244(9)	3.20(1)
Co····B1	5.515(9)	6.51(1)
O1····O2	2.472(9)	2.45(1)
O3····O4	2.524(9)	2.54(1)
N1−Co−N2	98.7(4)	97.8(7)
N1−Co−N3	82.2(3)	81.2(6)
N1−Co−N4	177.8(3)	173.8(5)
N2−Co−N4	82.3(3)	80.3(6)
N2−Co−N51	90.8(3)	92.8(5)
N3−Co−N4	96.7(3)	100.1(6)
N3−Co−N51	91.9(3)	92.7(5)
N4−Co−N51	90.8(3)	95.0(5)
N1−Co−C14	86.5(4)	87.4(6)
N2−Co−C14	85.8(4)	88.5(7)
N3−Co−C14	91.6(4)	86.0(6)
N4−Co−C14	91.8(4)	86.7(6)
N51−Co−C14	175.4(4)	178.1(6)
B····Co····B1	68.2(4)	83.2(6)
Co····B····Co1	111.8(4)	96.8(5)

Scheme 2



It was already reported that 4-pyridinyl boronic acid is a zwitterionic species[6] (Scheme 2). Spectrophotometric titrations showed two well-separated acid−base processes, with good isosbestic points at 210 and 260.2 nm, in the pH range 11.0−6.0, and at 256 nm, in the pH range nm 5.0−2.0, respectively. The relative pK_a values are 3.83 ± 0.05 and 8.2 ± 0.1, which are in fair agreement with the previously reported values (3.6 and 7.9).[6] The lower value was assigned to the ionization of the $B(OH)_2$ group, in view of the fact that a close pK_a value (4.4) was found for the ionization of *N*-methyl-3-pyridinium boronic acid.[8] The higher pK_a value was consequently assigned to the deprotonation of the pyridinyl group.

The ^{1}H, ^{13}C, and ^{11}B spectra in D_2O were strongly affected by the pH of the medium (see Experimental Section); in particular, the chemical shift of the pyridine protons were shifted remarkably upfield in basic medium (pH ≥ 9), confirming that deprotonation of pyridine occurs at these pH values, and at neutral pH, 4-pyridinyl boronic acid exists in aqueous solution mostly in the zwitterionic form.

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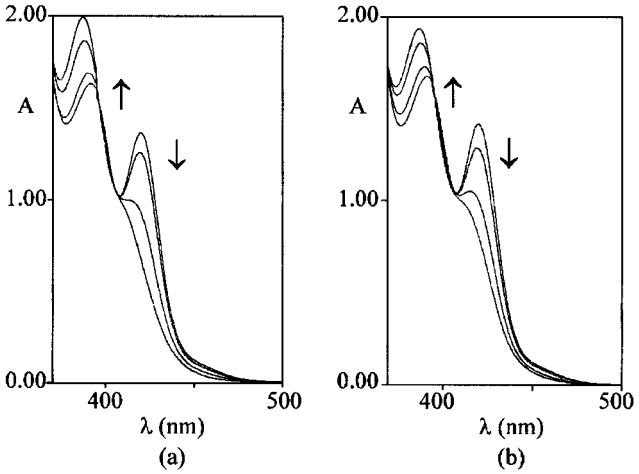


Figure 1. Comparison of spectral variation induced by coordination of 4-PyB$(OH)_2$ (a) and Py (b) at pH 10.

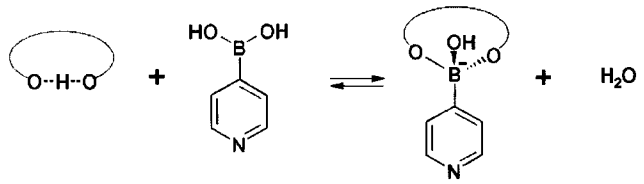
Reaction of $CH_3CO(DH)_2H_2O$ with 4-Pyridinyl Boronic Acid. The products of the reaction of cobaloxime with 4-pyridinyl boronic acid are strongly pH dependent. Addition of 4-pyridinyl boronic acid to $CH_3Co(DH)_2H_2O$ (1:1) in CD_3OD at pD about 10 caused a small shift of the signals in the ^{1}H NMR spectrum, comparable with those observed in the axial ligation processes. Only one signal was observed for the equatorial methyls, so insertion of a single boryl bridge could be excluded. The UV−visible studies confirmed the ligation of pyridine at this pH value; stepwise addition of 4-pyridinyl boronic acid to $CH_3Co(DH)_2H_2O$ in aqueous solution buffered at pH 10 caused spectral variations very similar to those due to the coordination of pyridine to $CH_3Co(DH)_2H_2O$ (Figure 1).

When the pD of the solution in CD_3OD was lowered to about 7 by addition of perchloric acid, a yellow compound, insoluble in methanol, but soluble in chloroform and CH_2Cl_2, deposited from the solution in the NMR tube. ^{1}H NMR spectra of this compound in $CDCl_3$ showed two singlets for the equatorial methyls, confirming the insertion of a single boryl bridge and a remarkable upfield shift of the pyridinyl protons. The UV−visible spectrum at pH 7 showed that pyridine was still coordinated. These results suggested that the complex obtained at pH 7 was a dimer similar to that previously obtained from the reaction of $CH_3Co(DH)_2H_2O$ with 3-pyridinyl boronic acid,[2] but with the pyridine rings facing each other and not coplanar. This justifies the notable upfield shift of the pyridinyl protons, which fall within the shielding cone of the pyridinyl group facing them.

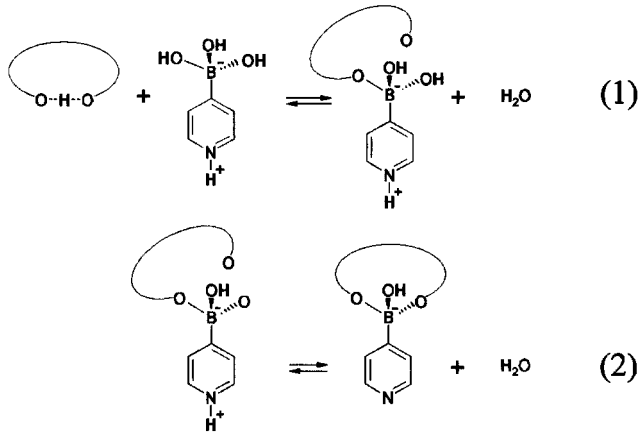
The preparative scale syntheses of the complexes were performed at pH 6.5 both in methanol (complex **2**) and water (complex **3**); the products were characterized by ESI−MS and NMR spectroscopy. The ESI−MS spectrum of a CH_3CN solution of **2** containing 1% formic acid gave $m/z^+ = 847$, corresponding to a dimer with both of the residual OH groups of the boronic acid esterified by methanol. The ^{1}H NMR spectrum in $CDCl_3$ of this complex showed one signal at 3.23 ppm, and the ^{13}C spectrum had a corresponding peak at 50.63 ppm, which were absent in the spectra of **3** and attributed to the OCH_3 group. An analogous esterification has been evidenced in the formation of **1** from $CH_3Co(DH)_2H_2O$ and 3-pyridinyl boronic acid in CH_2Cl_2/CH_3OH.[2]

The interaction of boronic acids with the diol functionalities of carbohydrates is well known.[9] The complexation of boronic acids by the O··H··O frame of bis(dimethylglyoximato) derivatives strongly resembles this interaction, but whereas the boronic

Scheme 3



Scheme 4



acid−diol complexes are stable in a more or less alkaline medium,[10] the formation of **2** requires a neutral medium. It has been shown that the formation of a hydroxyboronate species containing a tetrahedral boron is essential to strong binding in the boronic acid−diols complexes in aqueous solution.[11] The neutral pH values required for the formation of **2** and **3**, in methanolic or aqueous solvents, respectively, suggest that the reaction could involve the neutral form of the acid (Scheme 3) with loss of one molecule of water; more probably, the reaction involves the zwitterionic form of the acid (Scheme 4), with loss of a water molecule in a first step, deprotonation of pyridine, which in this way becomes available for coordination, and, finally, loss of a second water molecule. The lack of reactivity of the anionic form of the 4-pyridinyl boronic acid may be rationalized considering that the O··H··O frame of $CH_3Co(DH)_2H_2O$ contains only one proton and not two, as is the case for the diols. Consequently, the formation of the complexes from the anionic form of the acid should require the release of an OH^- group, which is clearly a disfavored process in alkaline medium.

X-ray Structure of (2). The crystal of **2** is built up by dimeric units arranged on a crystallographic symmetry center, so that the 4-pyridinyl group of one unit axially coordinates the Co atom of the symmetry related moiety. (Figure 2). A methanol molecule (occupancy factor, o.f. = 0.33), formic acid molecule (o.f. = 0.50), and five water molecules (o.f. = 0.33) were located in the crystal by Fourier-difference maps. The crystallization molecules are involved in a reciprocal H bond and anchored to the complex by the contact O1M ····O2 of 3.04(2) Å. The Co, B, Co1, and B1 atoms are at the vertexes of a slightly distorted rectangle. Each pyridine is nearly perpendicular to their mean plane (89.3°) and faces the symmetry related residue, with an

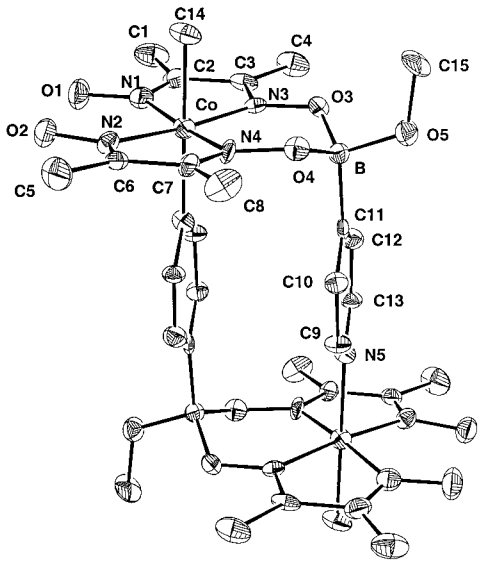


Figure 2. ORTEP drawing (thermal ellipsoid; 30% probability) and labeling scheme for the independent atoms in $[CH_3Co(DH)(DB(OCH_3)4-Py)]_2$ (**2**). The crystallization solvent molecules are not reported.

interplanar distance of 3.3 Å. Since the pyridinyl groups are also approximately perpendicular to the equatorial moiety (88.4°), the compound **2** can be considered to be a rectangular box. A dimeric arrangement has already been found in the related $[MeCo(DH)(DB(OMe)(3-Py))]_2$ (**1**) complex,[2] whose tetradentate ligand differs from that of **2** by having a 3-pyridinyl group on B. In the latter complex, the two pyridine residues, related by a symmetry center, are coplanar within 0.2 Å and approximately lie in the plane of the Co B Co1 B1 atoms. The latter atoms are at the vertexes of a parallelogram, whose mean plane makes an interplanar angle of 1.53° with the pyridinyl groups. Sketches of the dimers **1** and **2** are compared in Scheme 1, which shows how dimerization occurs in both cases by exploiting the conformational freedom (up or down) of the B bridge to compensate for the different position of the pyridinyl N donor. In fact, in **2** the pyridinyl ligand is in the axial position, whereas in **1** it is in the equatorial position. Nevertheless, the Co·····Co distances in **1** and **2** are very close, 7.365(3) and 7.592(5) Å, respectively. Furthermore, the axially coordinated pyridinyl ligand in **2** is oriented in such a way as to nearly bisect the five-membered rings of the equatorial moiety (dihedral angle C91−N51−Co−N1 of 40.9(5)°), whereas in **1** it is rotated by about 90° (dihedral angle of 128.7(4)). The latter orientation (orientation A) of the planar axial ligand is typical of octahedral cobaloximes and mono diphenylborylated cobaloximes, in which one H bridge has been formally replaced by a BPh_2 group.[12] The orientation in **2** (orientation B) is typical of iminocobaloximes (Costa's models) and of bis diphenylborylated cobaloximes. It has been observed that orientation A corresponds to shorter Co−N axial distances by about 0.03−0.04 Å.[3,12] However, such lengthening of the Co−N51 distance in **2** (2.08(1) Å) with respect to that (2.068(8) Å) in **1** is not apparent, probably owing to the relatively low accuracy of the present structural determination due to the large amount of the disordered solvent molecules. The cobalt in **2** has a distorted octahedral coordination with four nitrogens of the planar ligand in equatorial position; the axial positions are occupied by a methyl group and a pyridine of the symmetry related moiety. The comparison of the coordination bond distances and angles in **1** and

(9) For general reviews on boronic acid based saccharide receptors, see: a) James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1911. (b) James, T. D.; Linnane, P.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1996**, 281.

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2 is reported in Table 2. The cobalt atom is displaced by 0.10(5) Å and 0.03(6) Å out of the equatorial plane toward the axial pyridinyl in **2** and **1**, respectively. This difference, if significant, may be due to dimerization requirements. The boron atom is displaced 0.55(2) Å out of the six membered ring toward the axial N(py). This geometry contrasts with that observed in **1**, where the B atom is displaced by 0.61 Å toward the axial Me group.

Conclusions

3- and 4-PyB$(OH)_2$ act as templates in assembling dinuclear complexes from methylaquacobaloxime units by exploiting the equilibrium interactions of pyridine with the metal center and of boronic acid with the oxime bridges.[13] The product of the reaction with 3-PyB$(OH)_2$ may be considered a "molecular parallelogram", whereas that of the reaction with 4-PyB$(OH)_2$ is molecular box. In both cases, the dimerization occurs by exploiting the conformational freedom of the boron bridge to compensate for the different position of the pyridinyl N donor.

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Supporting Information Available: One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pub.acs.org.

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(13) An example of supramolecular assembly generated from metalloporphyrins and 3-pyridinylboronic acid has been reported. Sarson, L. D.; Ueda, K.; Takeuchi, M.; Shinkai, S. *J. Chem. Soc., Chem. Comm.* **1996**, 619.